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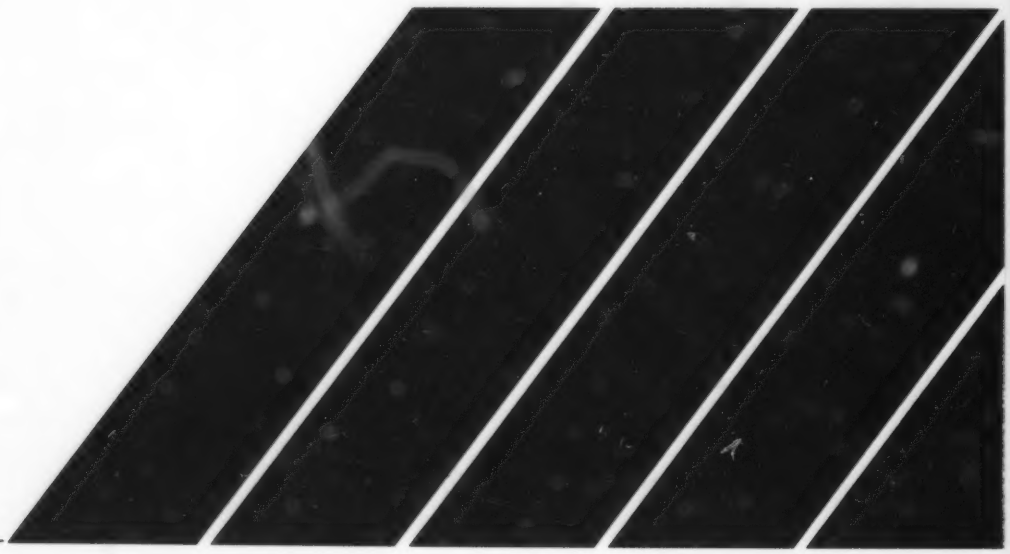
VACUUM PYROLYSIS OF BARK RESIDUES AND CLARIFIER SLUDGES: PHASE I



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VACUUM PYROLYSIS OF BARK RESIDUES AND CLARIFIER SLUDGES: PHASE I

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PREFACE

The disposal of bark residues and clarifier sludges produced by the pulp and paper sector has become one of the most important and urgent problems this industry is now facing in Canada. For example, la Commission d'enquête sur les déchets dangereux, set up by the Quebec Government in 1988, indicated that for the province of Quebec alone, pulp and paper plants generated 637,000 t/y of clarifier sludges (boues primaires) and 511,000 t/y of bark residues (résidus d'écorces) in 1989. These two waste streams represent approximately 70% by weight of all the wastes generated by the sector.

Vacuum pyrolysis is a technology which has been under development in Canada since the early 1980s. The process enables the thermal decomposition of organic wastes to pyrolysis oils and charcoal. It has been successfully applied to biomass feedstocks such as wood and to used tires. The idea behind this study is to explore the possibility of converting pulp and paper wastes such as bark residues and clarifier sludges into useful products. If technically and economically feasible, this project could very positively contribute to the industrial sector and simultaneously alleviate a growing environmental problem.

RÉSUMÉ

L'élimination des déchets d'écorçage et des boues de clarificateur produits par le secteur des pâtes et papiers est devenu l'un des problèmes les plus graves et les plus urgents auxquels fait face ce secteur de l'industrie au Canada. Ces deux types de déchets représentent, en termes de poids, environ 70 % de tous les déchets produits par l'industrie des pâtes et papiers.

La technologie de la pyrolyse sous vide fait l'objet de recherches au Canada depuis le début des années 80. Ce procédé permet la décomposition thermique des déchets organiques pour produire des huiles et du charbon de bois pyrolytiques. Il a été appliqué avec succès à la transformation de biomasses comme le bois, de même qu'à la récupération de pneus usés.

La présente étude a pour but d'explorer la possibilité de convertir en produits utiles des résidus de pâtes et papiers tels des déchets d'écorçage et des boues de clarificateur au moyen de procédés thermiques. La pyrolyse constitue une solution de rechange potentielle aux méthodes conventionnelles d'élimination de ces résidus, soit le compostage, l'incinération et la décharge contrôlée. Si l'on peut démontrer la faisabilité technique et économique du projet, sa réalisation pourrait se traduire par une contribution notable au secteur industriel et, par la même occasion, permettre de freiner l'expansion d'un problème environnemental grave.

Au cours de la présente étude, des échantillons de déchets d'écorçage et de boues de clarificateur prélevés à l'usine de pâtes et papiers Daishowa, à Québec, ont été soumis séparément à la pyrolyse sous vide au moyen d'un réacteur de laboratoire. L'écorce provenait de bois traité, principalement d'épinette noire, laquelle constitue 90 % du bois utilisé à l'usine. Parmi les autres espèces utilisées, on compte le pin gris, le sapin baumier, le peuplier faux-tremble et une faible proportion de bois durs de la famille des feuillus. Les déchets d'écorçage prélevés contenaient des matières inorganiques telles du sable, des roches et du métal, ainsi que des substances organiques telles des plastiques. Les boues de clarificateur obtenues de l'usine étaient composées des déchets lignocellulosiques résultant de l'ensemble des activités suivant l'étape de l'écorçage.

Le rapport documente les méthodes d'essai utilisées au cours des expériences sur la pyrolyse sous vide, et comporte des analyses détaillées des substances résultant du traitement de chaque échantillon.

ABSTRACT

Bark residues and clarifier sludge samples from the Daishowa pulp and paper plant in Quebec City have been processed by vacuum pyrolysis in a laboratory scale reactor system. The objective of the experimental study was to explore the possibility of thermally converting these pulp and paper wastes into useful products. Pyrolysis is a potential alternate solution to the conventional methods used for disposing of these materials, i.e. composting, incineration and landfill.

The two samples (approximately 5 kg each) of bark residues and clarifier sludges were collected by Carbovac Research Inc. at the Daishowa plant in January 1991. Bark originated from processed wood which is mainly black spruce. Black spruce accounts for 90% of all wood used in the plant. Other species include jack pine, balsam fir, aspen poplar and a small proportion of heavy hardwoods. Bark residues also contained inorganic matter such as sand, stones and metal, and organic substances like plastics. Clarifier sludges provided by the plant were the lignocellulosic wastes rejected from the entire plant operations, after the debarking stage.

The two samples were pyrolysed separately (each sample weighed approximately 1 kg) in a 10 L pyrolysis reactor by heating, under a 3-5 kPa absolute pressure, to a temperature of 486 °C. The pyrolysis product yields on an as-received basis were the following: clarifier sludges - oil, 40.05% / charcoal, 30.06% / pyrolytic water, 14.40% / gas, 11.71% / moisture, 3.78%; bark residues - oil, 30.62% / charcoal, 34.06% / pyrolytic water, 16.71% / gas, 14.44% / moisture, 4.17%. Clarifier sludges produced more oil, while more charcoal, pyrolytic water and gases were generated from the bark residues.

The oil phase from the bark-derived oil sample had a higher calorific value (7400 cal/g) compared to clarifier sludge-derived oil (6000 cal/g). The composition of the pyrolysis gases recovered from the two samples were similar, with an equivalent gross calorific value of about 1900 cal/g. Mainly due to its lower ash content, the bark charcoal had higher calorific value (6700 cal/g) than the clarifier sludge charcoal (5300 cal/g).

The oil phases recovered from the two pyrolysis experiments were fractionated and analyzed by GC/MS for compound identification. For the fractionation, 500 mg of each oil sample was transferred to an activated silica gel packed glass column of 300 mm long X 15 mm i.d., and the column was eluted with eight various solvents. Fractions 1 to 7 were analyzed.

Both pyrolysis oil samples had high contents of phenolic compounds which have potential usage in resin manufacture or as fuel additives. Various fine chemicals used in pharmaceutical products, insecticides, fungicides (furfural, creosol), disinfectants (xylenol), chemical reagents, and flavouring agents (vanillin, maltol) have been identified in both types of oils, which also contain about 2 - 4% of linear aliphatic hydrocarbons (C_{11} to C_{29}) and 2% of benzene derivatives or PAH. Long and short chain carboxylic acids were found in both oils, in relatively large quantities. Finally, it is suspected that a significant sugar content is present in these oils.

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VACUUM PYROLYSIS OF BARK RESIDUES AND CLARIFIER SLUDGES
PHASE I

1.0 INTRODUCTION

The objective of this work was to assess the potential of vacuum pyrolysis as a recycling process to transform pulp and paper waste materials to useful products such as oil and charcoal. Bark residues and clarifier sludges from "Les Produits forestiers Daishowa Inc." (Québec City) were the selected waste feedstocks. Both waste materials were separately studied in a laboratory scale reactor system. Composting, incineration and landfill are three methods currently used by the plant to dispose of this waste material. However, none of these methods is entirely satisfactory.

2.0 BARK RESIDUE AND CLARIFIER SLUDGE SAMPLES

The two samples (approximately 5 kg each) of bark residues and clarifier sludges were collected by Carbovac Research Inc. at the Daishowa plant in January 1991.

The bark originated from processed wood which is mainly black spruce. Black spruce accounts for 90% of all wood used in the plant. Other species include jack pine, balsam fir, aspen poplar and a small proportion of heavy hardwoods. Bark residues also contained inorganic matter such as sand, stones and metal, and organic substances like plastics. Clarifier sludges provided by the plant were the lignocellulosic wastes rejected from the entire plant operations, after the debarking stage. The bark sample was identified by the number B087-DAIECO, and the clarifier sludge sample by the number B086-DAICS.

The original moisture content of the two industrial residues was 66% and 60% for the clarifier sludge and the bark, respectively. The two samples were air-dried in the open at

room temperature for one week. They were then submitted to an elemental analysis and a proximate analysis for determination of the moisture, volatile matter and ash content, and the gross heating value. The results are compiled in Table 1.

Table 1: Clarifier Sludge and Bark Residue Samples Analyses

	Clarifier Sludges	Bark Residues
Moisture (%)	3.78	4.17
Proximate Analysis (dry basis):		
Ash (%)	8.83	2.29
Fixed Carbon (%)	14.72	21.69
Volatile Matter(%)	76.45	76.02
	100.00	100.00
Elemental Analysis		
C	50.35	54.15
H	6.02	6.25
N	0.49	0.36
S	0.81	0.07
O (by diff.)	42.33	39.17
	100.00	100.00
Gross Calorific Value ($MJ\ kg^{-1}$)	18	20

The moisture content was similar for both samples. The ash content of the clarifier sludge sample was higher (more than 6%) compared to that of the bark residue, while it was opposite for the fixed carbon percentage (7% less). The volatile matter contents are equivalent. The calorific value of both samples reflects the fixed carbon and volatile content.

3.0 EXPERIMENTAL

The two pyrolysis experiments, i.e. one for each sample, were conducted in a 10 L bench scale pyrolysis reactor (see Figure 1). A mass of 1 kg of clarifier feedstock was put in the reactor for the first run. The bark sample weighing approximately 1.2 kg was used for the second

run. The temperature in the reactor was raised at a rate of 2°C min^{-1} to a maximum temperature of 486°C in both tests, under a total pressure lower than 3.3 kPa for run B086, and 5.3 kPa for run B087. The pyrolysis products, liquids (oil, feedstock moisture and pyrolytic water) and charcoals, were weighed after each test, and the non-condensable gases were analyzed by gas chromatography. The pyrolysis liquid was composed of an oil phase with about 3% moisture (Table 2) and an aqueous phase containing also water soluble organic matter. Both phases are separable by decantation.

The moisture from the initial feedstock and the pyrolytic water mixes together and it is not possible to physically distinguish one from the other. The mass balance closures were satisfactory, at 99.8% and 100.6% for the two experiments, respectively. The yields are reported on a weight, as-received basis in Table 2 below.

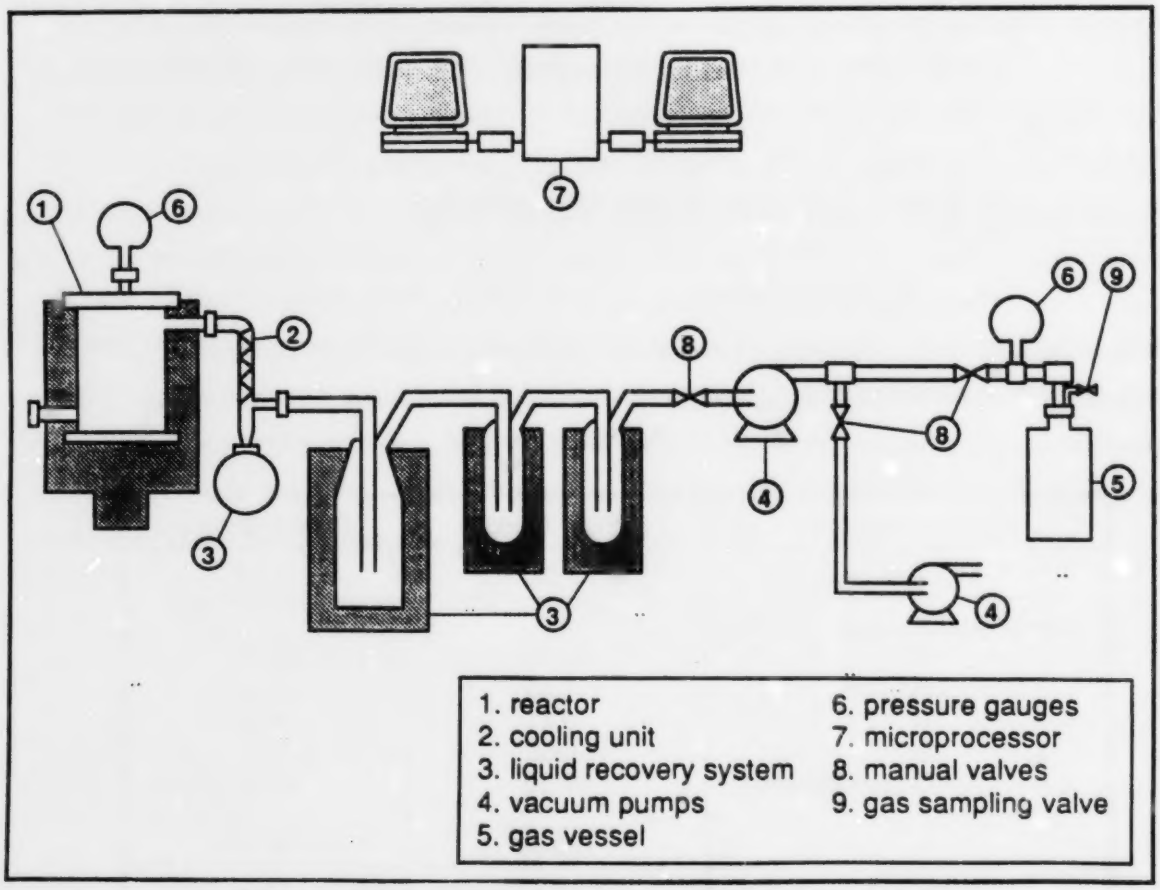

Figure 1 Schematic of the Batch Vacuum Pyrolysis System

Table 2: Yields on Vacuum Pyrolysis of Clarifier Sludges and Bark Residues (wt.%)

	B086	B087
	Clarifier sludges	Bark residues
Oils	40.05	30.62
Solid residues/ Charcoal	30.06	34.06
Pyrolytic water	14.40	16.71
Moisture	3.78	4.17
Gas	11.71	14.44
Total	100.00	100.00

The oil yield is remarkably high, especially for the clarifier sludge material. In both cases, the solid residues consisted of carbonaceous substances mixed with inorganic materials.

4.0 CHEMICAL ANALYSIS OF THE CONDENSATES

The oil phases from the two pyrolysis experiments have been analyzed for residual water content, gross calorific value and elemental composition. Results are presented in Table 3. No analysis of the aqueous phases was conducted during this investigation.

Table 3: Oil Phase Analysis

Chemical Analysis	Clarifier Sludges	Bark Residues
Moisture (%)	3.04	3.37
Elemental composition (wt.%)		
C	64.78	69.31
H	7.63	8.07
N	0.41	0.66
S	0.08	0.10
O (by difference)	27.10	21.86
	100.00	100.00
Gross calorific value (MJ/kg)	25.1	30.9

The pyrolysis oil phase from the bark sample has a higher calorific value compared to the one recovered from the clarifier sludge, which reflects the corresponding higher content in carbon and hydrogen.

What follows is a chemical analysis of the pyrolysis oils which has been conducted to identify the major compounds by a preparative liquid chromatography procedure, followed by a GC/MS analysis of the separated fractions.

4.1 Chemical analysis method

The brownish oil phase sample represented 42% by weight of the dry feedstock in the first case (clarifier sludges), and 32% for the other case (bark). The water content of each oil sample was determined by the Karl Fischer method.

The two oil samples were fractionated and each oil fraction was analyzed for compound identification. The analyses were made by means of a gas chromatograph coupled to a mass spectrometer (GC/MS).

Approximately 15 g of preliminary cleaned and activated silica gel (70-230 mesh, Aldrich) was packed in a glass column 300 mm long x 15 mm i.d. About 500 mg of oil sample was preadsorbed on 1 g of silica gel and then was transferred into the column. The column was eluted with various solvents. Tables 4 and 5 show the results for clarifier sludges and bark residues pyrolysis oils, respectively.

Table 4: Fractionation of Clarifier Sludges Pyrolysis Oil

Fraction	Eluent*	% Yield**
1	Petroleum Ether (P.E.)	4.2
2	25% Dichloromethane in P.E.	2.0
3	50% Dichloromethane in P.E.	4.4
4	75% Dichloromethane in P.E.	5.1
5	Dichloromethane	40.3
6	Ethyl Acetate	14.4
7	Methanol	26.8
8	10% Formic Acid in Methanol	8.9
		106.1

* 150 ml by fraction
** Anhydrous oil basis

Table 5: Fractionation of Bark Residues Pyrolysis Oil

Fraction	Eluent*	% Yield**
1	Petroleum Ether (P.E.)	2.0
2	25% Dichloromethane in P.E.	1.8
3	50% Dichloromethane in P.E.	4.5
4	75% Dichloromethane in P.E.	4.6
5	Dichloromethane	8.3
6	Ethyl Acetate	43.7
7	Methanol	26.5
8	10% Formic Acid in Methanol	8.0
		99.4

* 150 ml by fraction
** Anhydrous oil basis

The bark oil recovery yield was nearly 100% after fractionation. The overestimated yield of 106.1% in Table 4 (clarifier sludge oil) can be explained by the fact that methanol dissolves and elutes some silica gel. Also, complete removal of ethyl acetate, methanol and formic acid/methanol by evaporation is quite difficult.

All fractions shown in Tables 4 and 5 were analyzed by GC/MS. The operating conditions were the following:

GC/MS conditions: HP-5890 gas chromatograph with split injection mode (290°C) and helium carrier gas with about 1 ml · min^{-1} flow rate equipped with 30 m x 0.25 mm i.d. capillary column coated with DB 1701 (J and W) with 0,32 µm film thickness. The GC initial oven temperature was 40°C for 2 min, then programmed at a rate of 5°C min^{-1} to 270°C. The end of the column was introduced directly into the ion source of a HP-5970 series quadrupole mass selective detector. Typical mass spectrometric operating conditions were as follows: transfer line 270°C, ion source 280°C and 70 eV ionization potential. Data acquisition was done with HP-UX chemstation software and NBS library data base. The mass range m/z = 30 - 600 Dalton was scanned every two seconds.

4.2 Pyrolysis oils analysis

4.2.1 Clarifier sludge

Figures 2 and 3 show the total ion chromatograms of fractions 1 and 2, respectively. Several peaks have been identified in Tables 6 and 7. Fraction 1 consists mainly of linear aliphatic hydrocarbons. Alicyclic hydrocarbons and benzene derivatives are also present. Benzene and polycyclic aromatic hydrocarbons (PAH) derivatives are found in fraction 2. These two fractions correspond, respectively, to nearly 4% and 2% of the total dry oil (see Table 4).

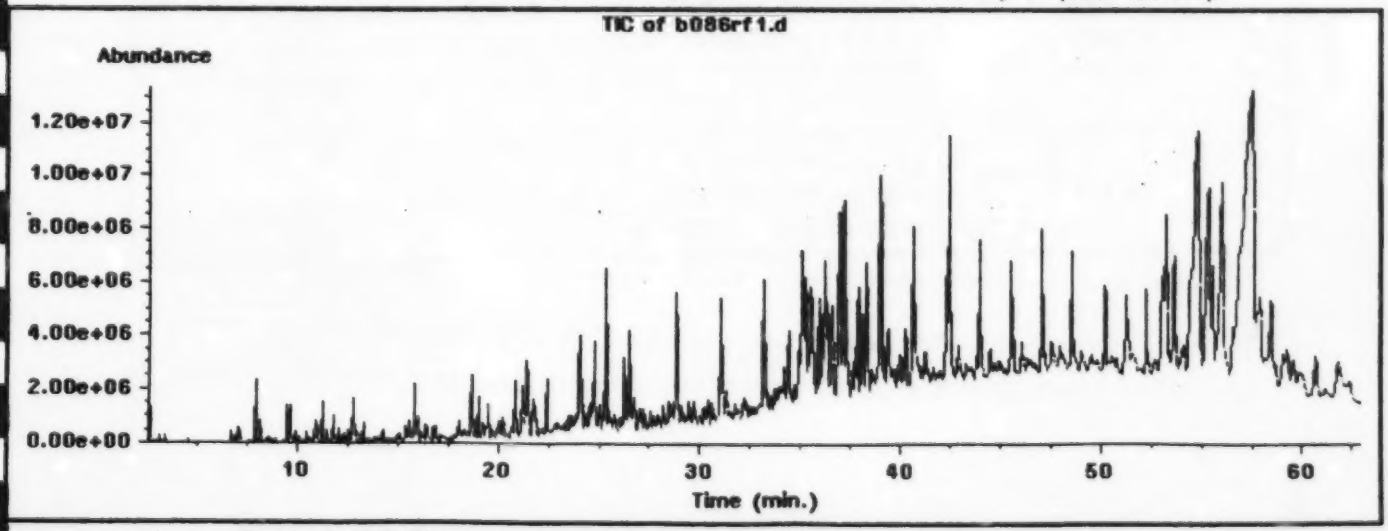

Figure 2 TIC Chromatogram of Clarifier Sludges Pyrolysis Oil Fraction #1

Table 6: GC/MS Analysis of Clarifier Sludges Pyrolysis Oil Fraction #1

Retention Time (min) (Figure 2)	Compound
9-50	Homologous series of n-alkanes and n-alkenes (C_{10} to C_{29})
7.100	1,2-Dimethylbenzene
7.929	3,6,6-Trimethyl-bicyclo[3.1.1]hept-2-ene
8.178	1,3,5,7-Cyclooctatetraene
9.484	6,6-Dimethyl-2-methylene-(s)-bicyclo[3.1.1]heptane
9.878	1-Ethyl-2-methylbenzene or isomer
10.438	1,1-Dimethyl-2-(3-methyl-1,3-butadienyl)-cyclopropane
10.853	(1-Methylethenyl)-benzene or 1-propenylbenzene
10.978	1,2,3-Trimethylbenzene or isomer
11.206	D-Limonene
11.455	4-Methylene-1-(1-methylethyl)-cyclohexene
11.766	Methyl(1-methylethyl)-benzene or isomer
12.244	1-Methyl-4-(1-methylethyl)-1,4-cyclohexadiene
12.846	Butylbenzene
13.136	3-Methyl-6-(1-methylethylidene)-cyclohexene
13.261	1,2-Propadienylbenzene or 1H-indene or 1-ethynyl-4-methyl-benzene
14.236	Methyl(1-methylethenyl)-benzene
15.046	7-Methylbenzofuran
15.482	2-Methylbenzofuran or isomer
15.939	Pentylbenzene
16.354	1,1a,6,6a-Tetrahydro-cycloprop[a]indene or 3-methyl-1H-indene
16.437	(1-Methyl-2-cyclopropen-1-yl)-benzene or 1-Methyl-1H-indene
18.058	Naphthalene
20.054	1,1-Dimethyl-1H-indene
21.199	1 or 2-Methylnaphthalene
21.699	1-Ethylidene-1H-indene or 1-methylnaphthalene
21.824	1,2,3,4-Tetrahydro-1,1,6-trimethylnaphthalene or isomer
22.407	Decahydro-4,8,8-trimethyl-9-methylene[1S(1α,3aβ,4α,8aβ]-1,4-methanoazulene
26.224	Octahydro-1,9,9-trimethyl-4-methylene-1H-3a-7-methano-azulene
34.377	7-Ethenyl-1,2,3,4,4a,5,6,7,8,9,10,10a-dodecahydro-1,1,4a,7-tetramethylphenanthrene

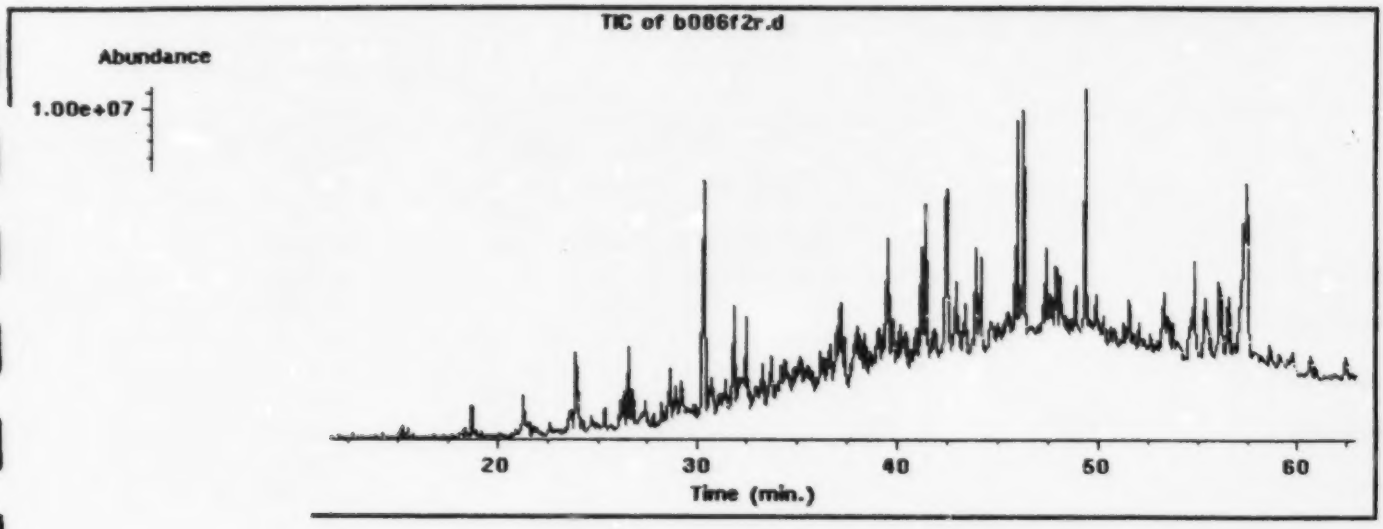

Figure 3 TIC Chromatogram of Clarifier Sludges Pyrolysis Oil Fraction #2

Table 7: GC/MS Analysis of Clarifier Sludges Pyrolysis Oil Fraction #2

Retention Time (min) (Figure 3)	Compound
23.616	2-Ethenylnaphthalene
23.928	8-(1-Methylethylidene)-bicyclo[3,2,1]oct-6-en-3-one
26.116	1-[4-(1,1-Dimethylethyl)phenyl]-ethanone or Ethylpentamethyl-benzene
28.913	1,4,6-Trimethylnaphthalene
29.205	9H-Fluorene
30.313	1,1'-(1,3-Propanediyl)bis-benzene
31.380	2,2'-Diethyl-1,1'-biphenyl
32.448	1-Methyl-3-(2-phenylethenyl)-benzene
37.168	2-Methylanthracene or 4 or 3-methylphenanthrene
39.544	2,7-Dimethylphenanthrene
41.459	2,3,5-Trimethylphenanthrene
42.491	1-Methyl-7-(1-methylethyl)-phenanthrene
42.954	1-(1,5-Dimethylhexyl)-4-(4-methylpentyl)-cyclohexane
43.418	2,4,5,7-Tetramethylphenanthrene

The chromatograms of fractions 3 and 4 are shown in Figures 4 and 5, respectively. The GC/MS analysis indicates that fraction 3 contains several phenol derivatives.

The compounds have been listed in Table 8. Fraction 4 is a mixture of phenols and furan derivatives. Some of them have been identified in Table 9.

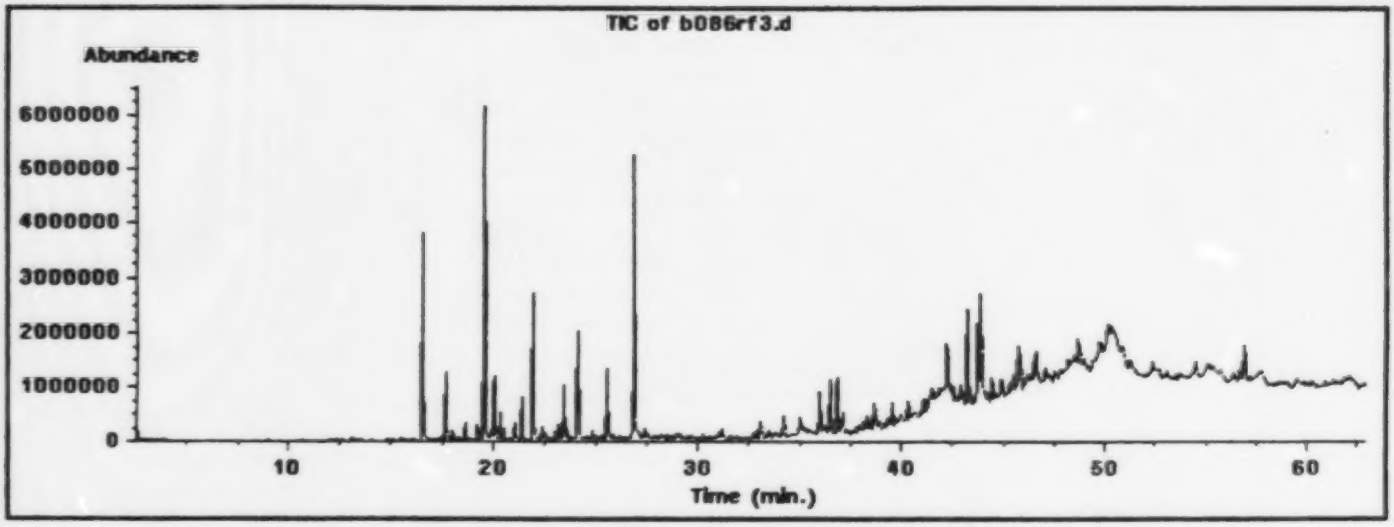

Figure 4 TIC Chromatogram of Clarifier Sludges Pyrolysis Oil Fraction #3

Table 8: GC/MS Analysis of Clarifier Sludges Pyrolysis Oil Fraction #3

Retention Time (min) (Figure 4)	Compound
16.545	4-Methoxyphenol
17.665	2-Methylphenol (cresol)
19.220	
19.552	2-Methoxy-4-methylphenol (creosol)
20.009	2,3-Dimethylphenol or isomer (xylenol)
20.320	1,4-Dimethoxy-2-methylbenzene
21.004	3,5-Dimethylphenol or isomer (xylenol)
21.896	4-Ethyl-2-methoxyphenol
22.353	4-Ethyl-3-methylphenol or isomer
24.095	2-Methoxy-4-(2-propenyl)-phenol
25.528	2-Methoxy-4-(1-propenyl)-phenol
26.856	2-Methoxy-5-(1-propenyl)-phenol
36.013	Oxacycloheptadecan-2-one
36.554	3-Ethenyldodecahydro-3,4a,7,7,10a-pentamethyl-[3S-(3α,4aα,6aβ,10aα,10bβ)]-1H-Naphtho[2,1-b]pyran
43.244	1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-7-(1-methyl-ethyl)-[1R-(1α,4aβ,10aα)]-1-phenanthrenecarboxaldehyde
43.892	1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl-7-(1-methyl-ethyl)-methylester-[1R-(1α,4aβ,10aα)]-1-phenanthrenecar-boxylic acid

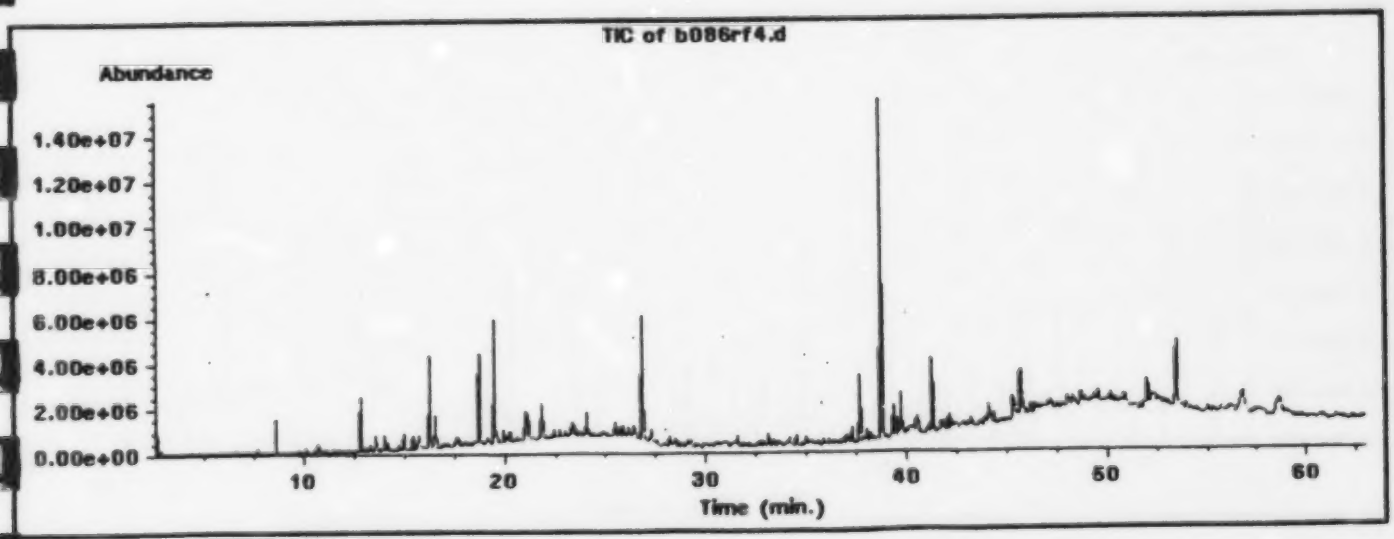

Figure 5 TIC Chromatogram of Clarifier Sludges Pyrolysis Oil Fraction #4

Table 9: GC/MS Analysis of Clarifier Sludges Pyrolysis Oil Fraction #4

Retention Time (min) (Figure 5)	Compound
8.561	2-Furancarboxaldehyde (furfural)
10.271	1-(2-Furanyl)-ethanone
12.819	5-Methyl-2-furancarboxaldehyde
16.209	Phenol (?)
16.480	4-Methoxyphenol
18.707	4-Methylphenol or isomer (cresol)
19.499	2-Methoxy-4-methylphenol (creosol)
21.020	3,5-Dimethylphenol or isomer (xylenol)
21.854	4-Ethyl-2-methoxyphenol
24.044	2-Methoxy-6-(1-propenyl)-phenol or isomer
26.819	2-Methoxy-4-(2-propenyl)-phenol
38.700	α-Ethenyldecahydro-α,5,5,8a-tetramethyl-2-methylene-[1S-[1α(S*),4aβ,8aα]]-1-naphthalenepropanol

The chromatogram of fraction 5, in Figure 6, shows many peaks. Unfortunately, only a few compounds, listed in Table 10, have been identified at this stage. This fraction amounts to 40% of the total dry oil and contains among other interesting compounds, a food aroma.

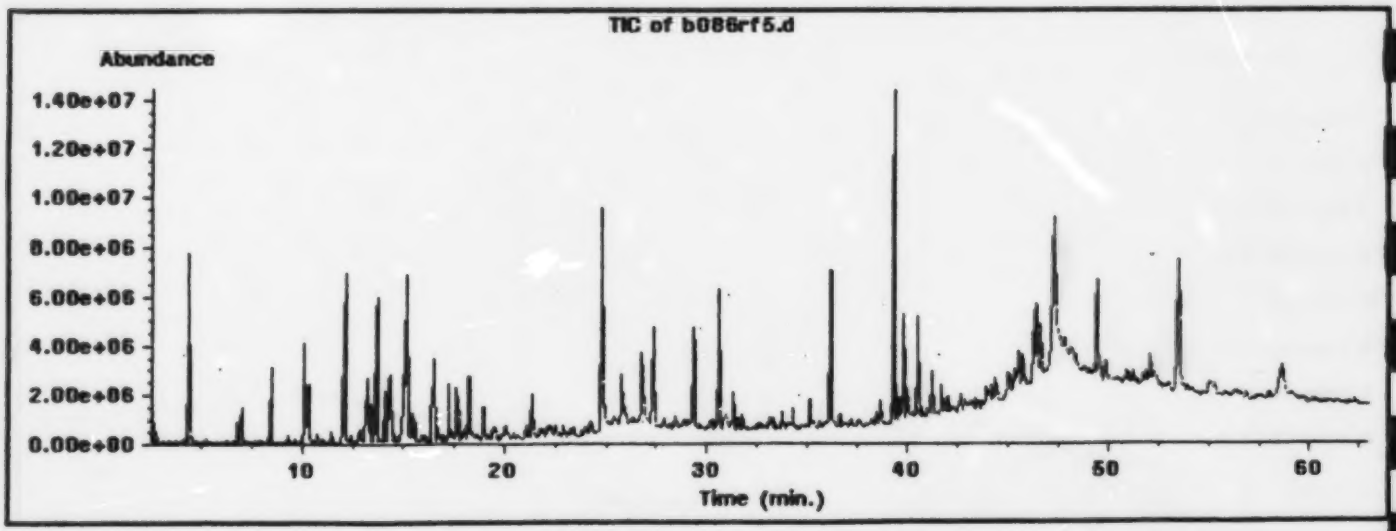

Figure 6 TIC Chromatogram of Clarifier Sludges Pyrolysis Oil Fraction #5

Table 10: GC/MS Analysis of Clarifier Sludges Pyrolysis Oil Fraction #5

Retention Time (min) (Figure 6)	Compound
8.459	2-Cyclopenten-1-one
10.120	2-Furanmethanol (furfuryl alcohol)
10.224	2-Methyl-2-cyclopenten-1-one
13.692	2(3H)-Furanone
17.247	2-Furancarboxylic acid hydrazide
25.720	3-Methyl-1,2-benzenediol
26.742	2-Methyl-1,3-benzenediol or isomer
27.326	4-Hydroxy-3-methoxybenzaldehyde (vanillin)
29.329	1-(4-Hydroxy-3-methoxyphenyl)-ethanone
47.482	1,2,3,4,4a,9,10,10a-Octahytdro-1,4a-dimethyl-7-(1-methyl-ethyl)-[1R-(1α,4aβ,10aα)]-1-phenanthrenecarboxylic acid

The chromatograms of fractions 6 and 7, presented, respectively, in Figures 7 and 8, show some large unresolved peaks. Those may be attributed to some carboxylic acids or their derivatives. Other peaks have been identified in Tables 11 and 12, respectively, and corresponded to short chain carboxylic acids and other highly polar compounds.

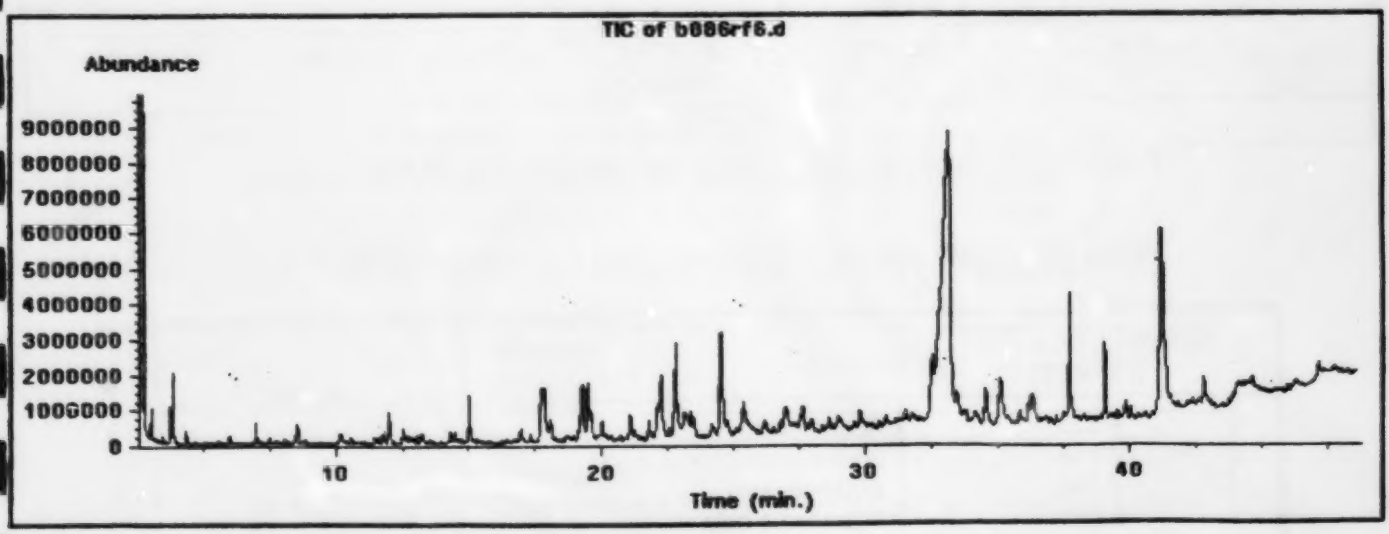

Figure 7 TIC Chromatogram of Clarifier Sludges Pyrolysis Oil Fraction # 6

Table 11: GC/MS Analysis of Clarifier Sludges Pyrolysis Oil Fraction # 6

Retention Time (min) (Figure 7)	Compound
3.749	Acetic acid
10.226	Isoerotonic acid
12.012	1,3-Cyclopentanedione
27.693	1,4-Benzenediol
37.732	Hexadecanoic acid
41.166	9-Octadecenal
41.250	9,17-Octadecadienal or 9,12-octadecadienoic acid

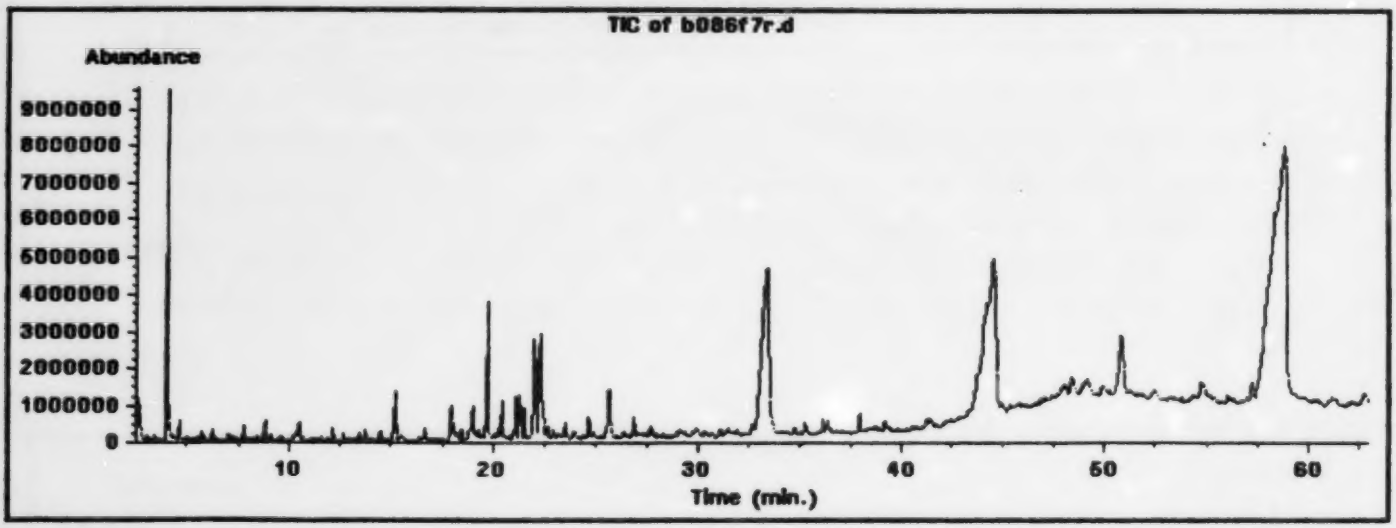

Figure 8 TIC Chromatogram of Clarifier Sludges Pyrolysis Oil Fraction # 7

Table 12: GC/MS Analysis of Clarifier Sludges Pyrolysis Oil Fraction # 7

Retention Time (min) (Figure 8)	Compound
4.015	Acetic acid
7.745	2-Methyl-propanoic acid
8.802	Butanoic acid
9.051	3-Butenoic acid
10.544	Isocrotonic or crotonic acid
17.864	Maltol
37.860	Octadecanoic acid

The remaining highly polar and high molecular weight compounds were eluted in fraction 8, but have not been characterized.

4.2.2 Bark residue

Like the clarifier sludges pyrolysis oil, the bark residues pyrolysis oil contained a small quantity of low polarity compounds. The chromatograms of fractions 1 and 2 are shown, respectively, in Figures 9 and 10. The compounds identified are listed in Tables 13 and 14 and correspond to linear aliphatic hydrocarbons and to polycyclic aromatic hydrocarbons (PAH). Both fractions represent about 2% of the dry oil (see Table 5).

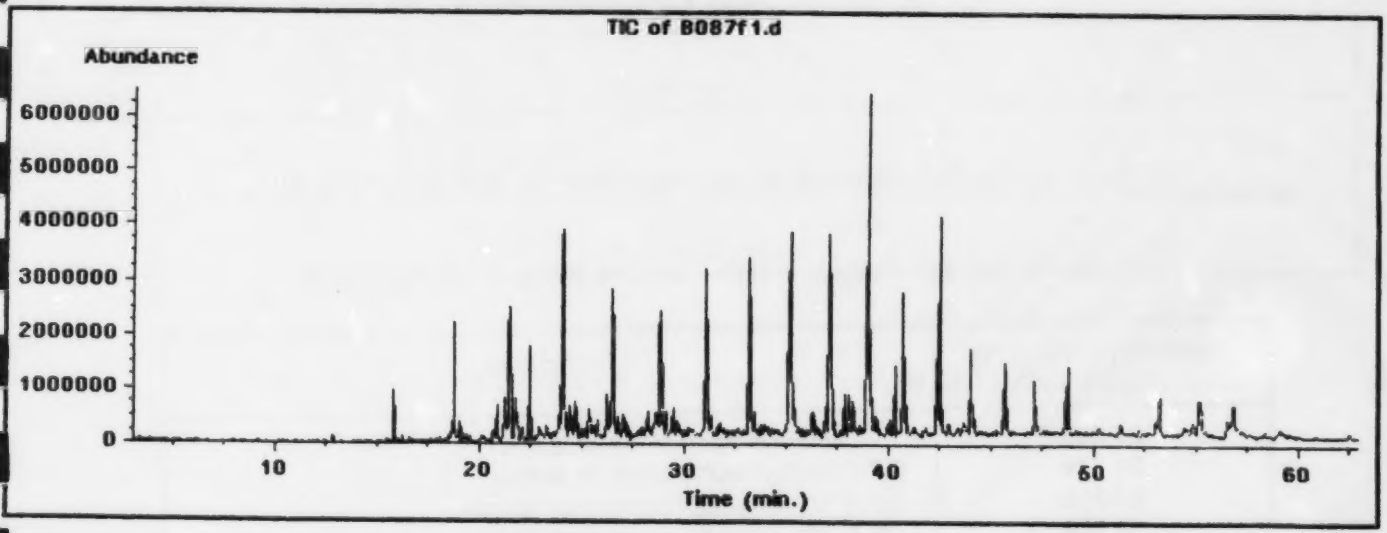

Figure 9 TIC Chromatogram of Bark Residues Pyrolysis Oil Fraction #1

Table 13: GC/MS Analysis of Bark Residues Pyrolysis Oil Fraction #1

Retention Time (min) (Figure 9)	Compound
15-50	Homologous series of n-alkanes and n-alkenes (C_{11} to C_{29})
21.254	1-Methylnaphthalene
22.465	Decahydro-4,8,8-trimethyl-9-methylene-1,4-methanoazulene (Longifolene)
24.700	1,6-Dimethylnaphthalene of isomer

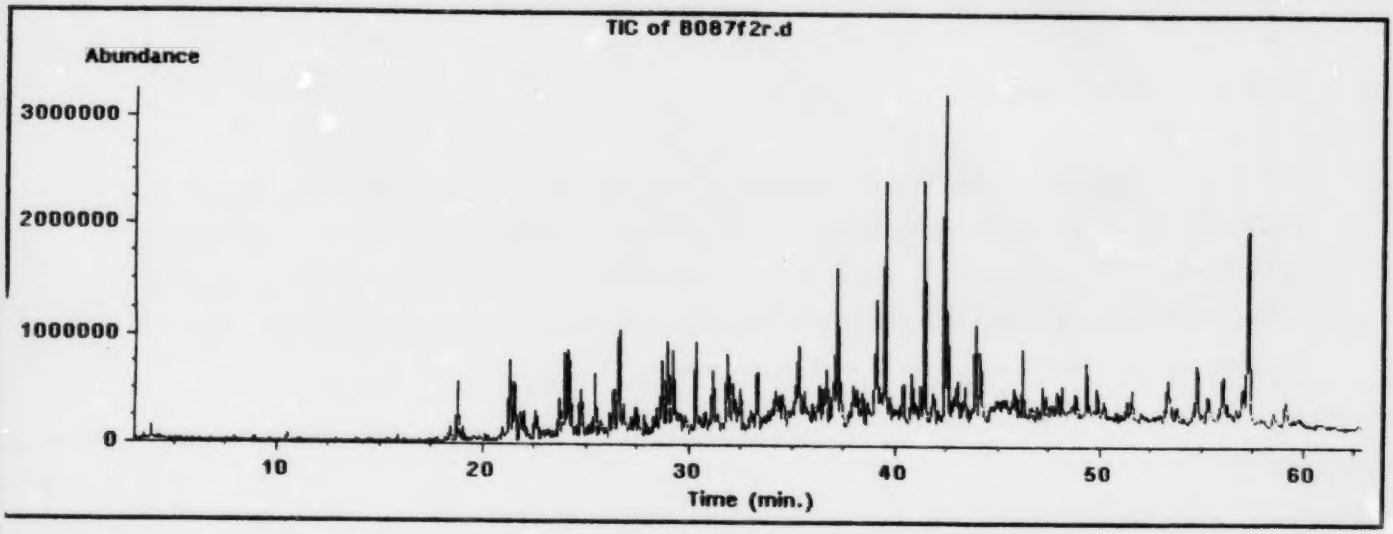

Figure 10 TIC Chromatogram of Bark Residues Pyrolysis Oil Fraction #2

Table 14: GC/MS Analysis of Bark Residues Pyrolysis Oil Fraction #2

Retention Time (min) (Figure 10)	Compound
24.696	1,3-Dimethylnaphthalene or isomer
24.779	2,7-Dimethylnaphthalene or isomer
27.412	2,3,6-Trimethylnaphthalene or isomer
28.959	1,4,6-Trimethylnaphthalene or isomer
29.231	9H-Fluorene
31.845	2-Methyl-9H-fluorene or isomer
32.117	4-Methyl-9H-fluorene or isomer
32.222	2-Methyl-9H-fluorene or isomer
34.188	Phenanthrene or anthracene or 9-methylene-9H-fluorene
37.184	2-Methylanthracene
39.531	2,5-Dimethylphenanthrene or isomer
42.465	2,4,5,7-Tetramethylphenanthrene

Figures 11 to 13 show the chromatograms of fractions 3 to 5, respectively. Several compounds have been identified and are presented in Tables 15 to 17. Most of them are phenol derivatives.

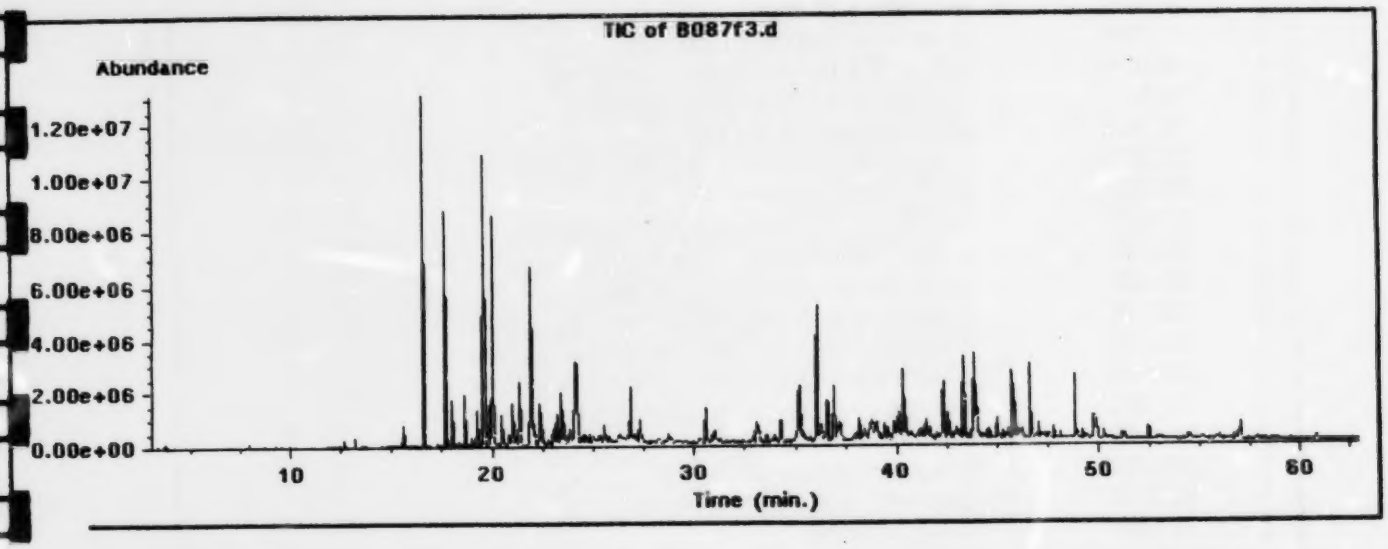

Figure 11 TIC Chromatogram of Bark Residues Pyrolysis Oil Fraction # 3

Table 15: GC/MS Analysis of Bark Residues Pyrolysis Oil Fraction #3

Retention Time (min) (Figure 11)	Compound
12.624	Methyl ester of furancarboxylic acid
15.625	Methyl benzoate
16.605	4-Methoxy phenol
17.769	2- or 4-Methylphenol (cresol)
18.024	2,5- or 2,6-Dimethylphenol (xylenol)
19.611	2-Methoxy-4-methylphenol (cresol)
19.882	2-Ethylphenol or isomer
20.045	2,4-Dimethylphenol or isomer (xylenol)
20.509	2,3,6-Trimethylphenol or isomer
21.031	3,5-Dimethylphenol or isomer (xylenol)
22.369	4-Ethyl-3-methylphenol or isomer
23.183	2,3,5-Trimethylphenol or isomer
24.125	2-Methoxy-4-(2-propenyl)-phenol or isomer
25.547	2-Methoxy-5-(1-propenyl)-phenol or isomer
26.864	2-Methoxy-4-(1-propenyl)-phenol or isomer
27.325	4-Hydroxy-3-methoxybenzaldehyde (vanillin)
35.143	8-Amino-2-naphthalenol
36.086	Oxacycloheptadecan-2-one
40.316	Oxacycloheptadec-8-in-2-one
47.022	1-Tetracosanol
47.776	Diacetate 1,1-dodecanediol

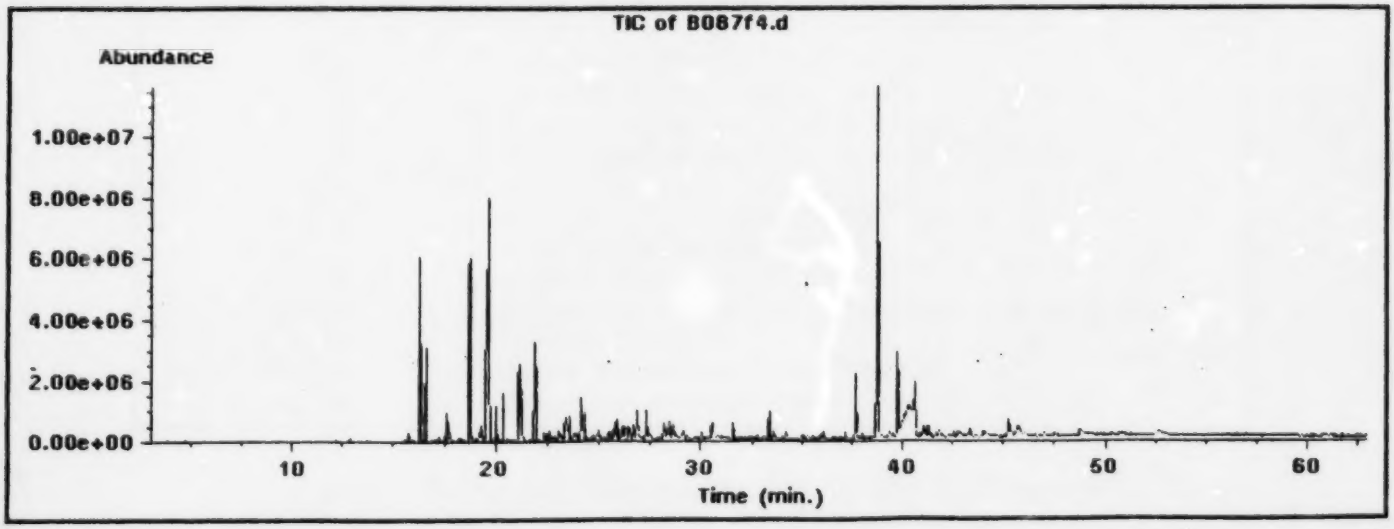

Figure 12 TIC Chromatogram of Bark Residues Pyrolysis Oil Fraction #4

Table 16: GC/MS Analysis of Bark Residues Pyrolysis Oil Fraction # 4

Retention Time (min) (Figure 12)	Compound
12.853	Δ5-Methyl-2-furancarboxaldehyde
16.269	Phenol
16.562	4-Methoxyphenol
17.666	4-Methylphenol or isomer (cresol)
18.772	3-Methylphenol or isomer (cresol
19.606	2-Methoxy-4-methylphenol (creosol)
20.023	2,4-Dimethylphenol or isomer (xylenol)
20.336	1,4-Dimethoxy-2-methylbenzene
21.087	3,5-Dimethylphenol or isomer (xylenol)
21.254	2-Ethylphenol or 2,3-Dimethylphenol
21.859	3,4-Dimethylphenol or 3-Ethylphenol
22.381	4-Ethyl-3-methylphenol
23.404	2-Ethyl-6-methylphenol
24.134	2-Methoxy-4-(2-propenyl)-phenol or isomer
25.553	2-Methoxy-4-(1-propenyl)-phenol or isomer
25.804	2,3-Dihydro-1M-inden-5-ol
25.929	1,3-Dihydro-5-methyl-2H-benzimidazol-2-one
26.222	Ethenylbenzaldehyde
26.869	2-Methoxy-5-(1-propenyl)-phenol
27.329	4-Hydroxy-3-methoxybenzaldehyde (vanillin)

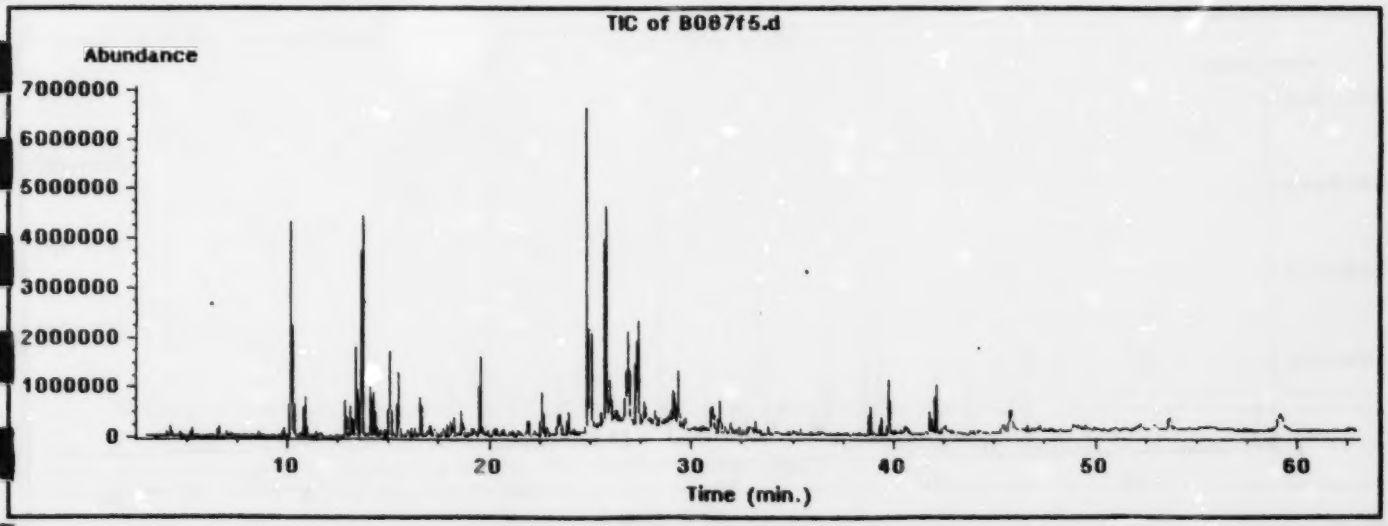

Figure 13 TIC Chromatogram of Bark Residues Pyrolysis Oil Fraction # 5

Table 17: GC/MS Analysis of Bark Residues Pyrolysis Oil Fraction #5

Retention Time (min) (Figure 13)	Compound
4.187	2-Pentanol
9.770	Cyclohexanone
10.166	2-Furanmethanol (furfuryl alcohol)
10.291	2-Methyl-2-cyclopenten-1-one
10.812	1-(2-Furanyl)-ethanone
12.875	5-Methyl-2-furancarboxaldehyde
15.043	3-Methyl-2(5H)-furanone
16.565	4-Methoxyphenol
18.713	4-Methylphenol or isomer
19.569	2-Methoxy-4-methylphenol (creosol)
22.593	2,3-Dihydro-1H-inden-1-one
24.993	2,6-Dimethoxyphenol
25.788	3-Methyl-1,2-benzenediol or isomer
27.377	4-Hydroxy-3-methoxybenzaldehyde (vanillin)

Fractions 6 and 7 are quite polar and amount to 70% of the anhydrous oil. The TIC chromatograms are shown in Figures 14 and 15. Some compounds have been identified in Tables 18 and 19, respectively.

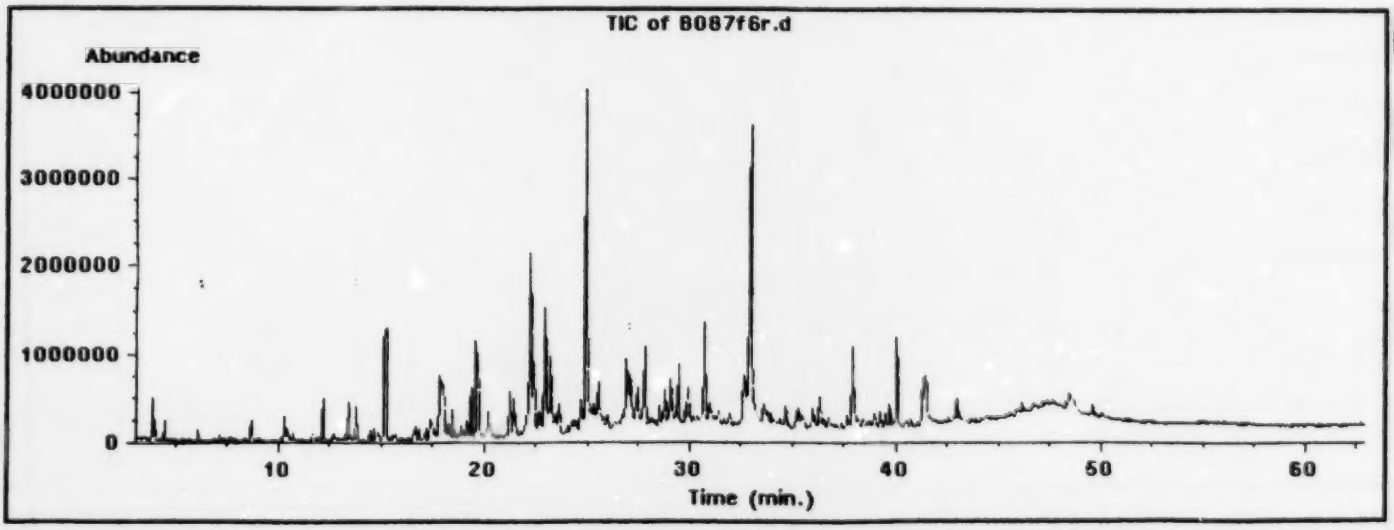

Figure 14 TIC Chromatogram of Bark Residues Pyrolysis Oil Fraction #6

Table 18: GC/MS Analysis of Bark Residues Pyrolysis Oil Fraction #6

Retention Time (min) (Figure 14)	Compound
4.439	1-Hydroxy-2-propanone (acetol)
15.170	2-Hydroxy-3-methyl-2-cyclopenten-1-one
21.408	Benzoic acid
24.895	1,2-Benzenediol (catechol)
26.881	3-Methyl-1,2-benzenediol or isomer
27.445	4-Hydroxy-3-methoxy-benzaldehyde or isomer (vanillin)
27.801	1,4-Benzenediol
28.804	5-Methyl-1,3-benzenediol
29.453	1-(4-Hydroxy-3-methoxyphenyl)-ethanone
37.899	Hexadecanoic acid
41.308	1-Tetradecanol
41.412	Methyl ester of 11,14-eicosadienoic acid

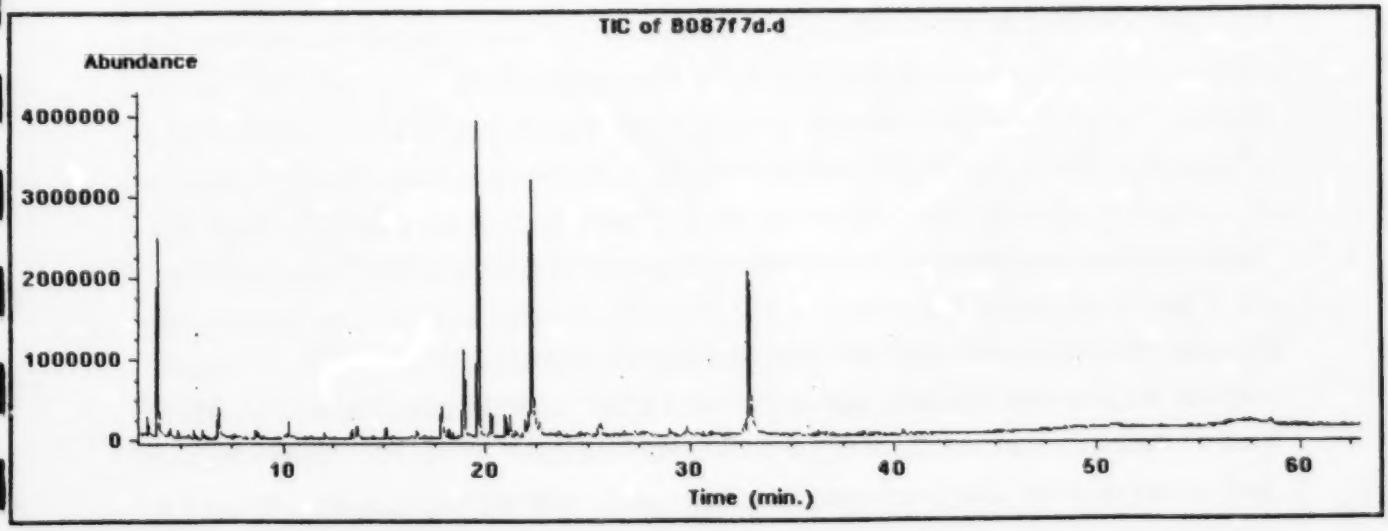

Figure 15 TIC Chromatogram of Bark Residues Pyrolysis Oil Fraction #7

Table 19: GC/MS Analysis of Bark Residues Pyrolysis Oil Fraction #7

Retention Time (min) (Figure 15)	Compound
3.813	Acetic acid
10.294	Crotonic acid
17.817	Maltol
32.895	Short chain carboxylic acids (probably)

Fraction 6 contains some diols and carboxylic acids. The fraction 7 chromatogram presents a broad unresolved peak which may correspond to short chain carboxylic acids. More highly polar and high molecular weight compounds were eluted in fraction 8 for which we have not made any analysis at this stage.

4.2.3 Discussion

Vacuum pyrolysis of clarifier sludges and bark residues gave high yields of interesting liquid products: 42% and 32% (wt %, feedstock dry basis) of pyrolytic oil from sludges and bark, respectively. Fractions 3 - 5 (49.8%) and 4 - 6 (56.6%) of the clarifier sludges and bark residue pyrolysis oils, respectively, are concentrated in phenolic compounds. Over 9% phenolics have been identified so far in both types of pyrolysis oils. It seems possible to separate the phenolic compounds and use them in bulk for the manufacture of resins or, alternatively, as fuel additives. Based on their order of elution from the liquid chromatographic column, the remaining compounds in the LC column are also expected to be of phenolic nature. The unambiguous assignments of these last polar compounds have not been made at this stage, due to the lack of standards and complementary instrumentation such as HPLC/MS and GC/FTIR. The oils are also a source of various fine chemicals that could be extracted and used, for example, as pharmaceutical products, insecticides and fungicides (furfural, creosol), disinfectants (xylenol), chemical reagents, and flavouring agents (vanillin, maltol). Both oils contain about 2% - 4% of linear aliphatic hydrocarbons (C_{11} to C_{29}) and 2% of benzene derivatives or PAH. Long and short chain carboxylic acids have been identified in both oils, in relatively large quantity. Finally it is probable that pyrolytic oils have a significant sugar content. This could be investigated in the future.

5.0 CHEMICAL ANALYSIS OF THE SOLID RESIDUES (CHARCOAL)

Vacuum pyrolysis of clarifier sludges and bark residues also gave high yields of charcoal products: 31% and 36% (wt. %, feedstock dry basis), respectively. Charcoals from the two pyrolysis runs have been characterized in terms of ash, gross calorific value, and proximate and elemental analysis. Results are summarized in Table 20.

Table 20: Solid Residues Analysis

	Clarifier Sludges	Bark Residues
Moisture (%)	0.59	0.46
Proximate analysis (wt %)		
Volatile Matter	24.54	20.48
Ash	32.64	15.86
Fixed Carbon	42.82	63.66
	100.00	100.00
Elemental analysis (wt %)		
C	81.78	87.69
H	3.03	3.29
N	0.98	1.02
S	3.49	0.20
O (by difference)	10.72	7.80
	100.00	100.00
Gross calorific value ($MJ\ kg^{-1}$)	22.2	28.1

The gross calorific value of the bark charcoal is higher than the clarifier sludge charcoal. The ash content is lower for the bark residue charcoal. The elemental analysis results are in line with the data for the calorific values.

6.0 CHEMICAL ANALYSIS OF THE NON-CONDENSABLE GAS PHASE

The non-condensable gas phases recovered during both experiments were analyzed by gas chromatography. Results presented in Table 21 show that the major single component is $C0_2$, followed by CO in both cases. The gross calorific values are low which was expected. The gas can provide a make-up heat source for the process itself.

Table 21: Pyrolysis Gas Composition (vol. %)

	B086 Clarifier sludges	B087 Bark residues
Hydrogen (H_2)	2.36	3.23
Methane (CH_4)	8.95	9.77
Carbon monoxide (CO)	36.16	29.79
Carbon dioxide (CO_2)	47.71	51.19
Ethene (C_2H_4)	0.83	0.78
Ethane (C_2H_6)	0.93	1.33
Propene (C_3H_6)	0.53	0.71
Propane (C_3H_8)	0.62	0.65
Acetaldehyde (CH_3COH)	0.69	0.74
Butene (C_3H_8)	0.21	0.29
Butane (C_4H_{10})	0.14	0.25
Acetone (CH_3COCH_3)	0.42	0.56
Others	0.45	0.72
	100.00	100.00
Average Molecular Weight (g mol^{-1})	34.67	35.17
Gross Calorific Value (MJ kg^{-1})	7.8	8.1

7.0 RESULT SUMMARY AND FINAL CONCLUSIONS

The main conclusions from this experimental study are the following:

- Vacuum pyrolysis to a temperature of 486 °C, and under an absolute pressure of 3-5 kPa, of air-dry bark residue and clarifier sludge samples in a 10 L bench scale reactor

produced substantial amounts of chemical-rich oils and charcoal. The yields on an air-dry, feedstock basis are:

Bark residues: oil, 30.62% / charcoal, 34.06% / pyrolytic water, 16.71% / gas, 14.44% / moisture, 4.17%.

Clarifier sludges: oil, 40.05% / charcoal, 30.06% / pyrolytic water, 14.40% / gas, 11.71% / moisture, 3.78%.

- The oil phase recovered from the pyrolysis of bark sample, as well as the charcoal from this feedstock, have higher gross calorific values than the clarifier sludge pyrolytic oil or charcoal:

	OIL	CHARCOAL
Bark Residue	7400 cal/g	6700 cal/g
Clarifier Sludges	6000 cal/g	5300 cal/g

- Composition of the pyrolysis gas phases is similar for both cases. Heating value of the gas phase is not high, however.

- Fractionation of both pyrolytic oil samples using eight various solvents for elution of a 500 mg oil sample in a 300 mm X 15 mm i.d. packed column, followed by compound identification with GC/MS equipment, revealed a high content in phenolic compounds for both oils. Both samples also contained approximately 2 - 4% linear aliphatic hydrocarbons (C_{11} to C_{29}) and 2% of benzene derivatives or PAH. Long and short chain carboxylic acids have been identified in the two types of oils, in relatively large quantities. The oils are also a source of various fine chemicals that could find applications in pharmaceutical products, insecticides, fungicides, desinfectants, chemical reagents, and flavouring agents.